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Title: Development of an Experimental Database and Theories for Prediction of Thermodynamic Properties of Aqueous Electrolytes and Nonelectrolytes of Geochemical Significance at Supercritical Temperatures and Pressures

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Executive Summary

The reactions that cause transformations in organic compounds in the Earth's crust remain mysterious despite decades of research into how fossil fuel resources form. A major reason for this persistent mysteriousness is the failure of many researchers to realize the intimate involvement of water in those transformations. Our goal was to overcome this staggering ignorance by developing the means to calculate the consequences of reactions involving organic compounds and water. We pursued this research from 1989 through 2006, and this report focuses on progress between 2002 and 2006. There were two major obstacles that we overcame in the course of this research. On the one hand, we developed new theoretical equations that allow researchers to make these calculations. On the other hand, we critiqued available data and provided sound means to make estimates in the absence of experimental data for hundreds of organic compounds dissolved in water. Finally, we merged these two lines of research into an interactive web site that allows users to do the calculations with the equations and data. We call the web site ORCHYD for: "ORganic Compounds HYDration properties database," but it is far more than a database since it allows users to make extremely accurate predictions of data that may never have been measured. Our progress greatly exceeded our anticipations, and has permitted many new research investigations that were previously impossible. Despite the abrupt termination of funding for this project by the Department of Energy, we are maintaining the web site for the international scientific community. Major research results were published in eleven scientific papers, so they are all in the public domain. Benefits to the public include a new, rigorous, quantitative approach to testing ideas about the fate of organic compounds dissolved in water. These tests can be applied to geochemistry or to industrial processes. The increasing use of water as a solvent in Green Chemistry and Sustainable Industrial Practices, means that there is a pressing need for data and calculations of the type we have provided and enabled. Applications include: improved efficiency of industrial processes, improvements in health protections for workers who encounter organic solvents and other organic compounds, predictive tools for cleaning up landfills and other toxic waste, and the potential for a greater understanding of how petroleum forms.

OBJECTIVES: The objectives of this research were to combine new experimental measurements on heat capacities, volumes, and association constants of key compounds with theoretical equations of state, and with first principals quantum mechanical predictions, to generate estimates of thermodynamic properties of aqueous solutes. The resulting thermodynamic data allow new quantitative models of geochemical processes at high temperatures and pressures.

PROJECT DESCRIPTION: This project grew out of a long-standing collaboration between Prof. Everett Shock of Arizona State University and Prof. Robert Wood of the University of Delaware, which was funded by DOE from 1989-2006 and involved
1) experimental measurements on key compounds
2) making substantial improvements in theoretical equations of state for aqueous nonelectrolytes and electrolytes based largely on these experimental measurements
3) pursuing novel applications of these equations of state to the study of high temperature/pressure geochemical processes involving aqueous fluids, and
4) developing and using *ab initio* quantum calculations with molecular dynamics simulations to predict chemical potentials of aqueous solutes where experimental measurements are impossible or not available.
The experimental work was conducted at the University of Delaware. Geochemical applications of the data were done at Arizona State University (ASU). Efforts to improve the equations of state and develop predictive methods were shared between the two labs, because this task in particular required close collaboration between the Principal Investigators.

RESULTS: Progress at ASU accomplished with the funding supplied by this grant includes analysis and critique of thermodynamic data, development of estimation methods, and exploration of new equations of state for nonelectrolytes. **This research progress exceeded the goals of the original proposal.**

Dr. Andrey Plyasunov completed a study of second cross virial coefficients and cross Joule-Thomson coefficients for interactions involving water. This project involved assembling all of the relevant experimental data from which these coefficients can be calculated, developing methods to extrapolate and estimate these coefficients, and working out a group contribution scheme for aqueous organic nonelectrolytes. Two papers were completed and submitted (Plyasunov and Shock, 2003a; and Plyasunov et al., 2003).

We also concentrated on further developments of our Fluctuation Solution Theory (FST) based models for aqueous species. In their current form FST formulations can be applied to neutral solutes, given values of the second cross virial coefficient with water. Now that such coefficients can be more reliably estimated, we made renewed progress with the FST approach (Plyasunov et al., 2007).

In addition, work progressed on methods to predict vapor-liquid distribution constants up to the critical temperature of water for many aqueous solutes. For many geochemical applications, values of the vapor-liquid distribution constants are needed for quantitative modeling of the fate of chemical constituents when fractionation

between liquid and vapor phases occurs. There are many suggestions in the literature that boiling can have dramatic effects on the evolution of hydrothermal solutions, but sound numerical approaches are uncommon. We provided the means to calculate the distribution constants for many inorganic species and obtained values for organic functional groups as well (Plyasunov and Shock, 2003b). Related work produced a new means for estimating Krichevskii parameters for volatile nonelectrolytes in water (Plyasunov and Shock, 2004)

Together with Dr. Natalia Plyasunova, we also made major progress in developing group-contribution methods for estimating standard state thermodynamic data for aqueous organic solutes. This work produced results for aliphatic esters (Plyasunov et al., 2004); aliphatic thiols, alkyl sulfides, and polysulfides (Plyasunova et al., 2005); aliphatic monoethers, diethers, polyethers (Plyasunov et al., 2006a); and aliphatic nitriles and dinitriles (Plyasunov et al., 2006b). In parallel, we built, documented (Plyasunova et al., 2004) and maintained an interactive web site that supports estimation of thermodynamic data using our group-contribution methods (**http://orchyd.asu.edu/**).

Progress was also made in applying these new data in geochemical model calculations. Results for seafloor hydrothermal systems (Shock and Holland, 2004) provide quantitative links between geochemical and biological processes based on the energy released during autotrophic metabolism. Additional results were presented in talks and posters at national and international meetings. The decision by DOE to stop funding this research has slowed the appearance of corresponding papers.

Publications

Plyasunov, A.V. and Shock, E.L. (2003a) Second cross virial coefficients for interactions involving water. Critical data compilation. *Journal of Chemical and Engineering Data* **48**, 808-821.

Plyasunov, A.V. and Shock, E.L. (2003b) Prediction of the vapor-liquid distribution constants for volatile nonelectrolytes in H_2O up to the critical temperature of water. *Geochim. Cosmochim. Acta* **67**, 4981-5009.

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Plyasunov, A.V., Shock, E.L. and Wood, R.H. (2003) Second cross virial coefficients for interactions involving water. Correlations and group contribution values. *Journal of Chemical and Engineering Data* **48**, 1463-1470.

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Shock, E.L. and Holland, M. E. (2004) Geochemical energy sources that support the subseafloor biosphere. *The Subseafloor Biosphere at Mid-Ocean Ridges.* (Geophysical Monograph 144, Eds: W.S.D. Wilcock, E.F. DeLong, D.S. Kelley, J. A. Baross, S.C. Cary) American Geophysical Union, pp. 153-165.

Web Site

http://orchyd.asu.edu/